## Dynamic Reduction and the Creation of Fine-Grained Ceramics from Inviscid Oxide/Silicate Melts

Reid F. Cooper Department of Materials Science and Engineering University of Wisconsin 1509 University Avenue Madison, WI 53706 Phone: (608) 262-1133

E-mail: cooper@engr.wisc.edu

The overall materials science objectives of this research program are to discern, characterize, and develop a useful approach to the creation of fine-grained ceramics from inviscid (low-viscosity) ionic melts. The scientific problem centers on the need to control the density and spatial distribution of crystalline nuclei in such melts. We (my graduate students and I) have identified a new, unique "alternative" approach to controlled nucleation, for which microgravity containerless processing is required: dynamic reduction. In transition-metal-cation-bearing, multicomponent ionic melts, the redox dynamics are such that relatively rapid processing is possible.

Melts that contain multiple cations can be forced to undergo a dynamic reduction reaction, given appropriate control of the activity of oxygen of the process environment. In the case where a transition metal oxide component is a minority constituent of the melt, such a reaction can result in the uniform distribution of metal (either as fine crystals or as fine, discrete droplets, depending on the temperature) within the (now) transition-metal-cation-depleted ionic melt. Because of the presence of the transition metal cation species, the kinetics of the process involves the diffusive motion of cations that is charge-compensated by the rapid motion of electronic defects (i.e., polarons: localized electrons or electron holes); as such, reduction should occur at an internal front. (One objective of the research, then, is to characterize the morphology and possible variations of morphology of such reduction dynamics in melts.) In this approach, then, the finely and uniformly dispersed metal phase can act as a substrate for the heterogeneous crystalline nucleation of the remaining ionic melt upon its cooling. This reduction approach could prove effective, too, in controlling the coarsening of the metal nuclei: Ostwald ripening processes would require redox reactions at the metal/ceramic interface, which could be rate limiting. At present, we are pursuing control experiments on Fe<sup>2+</sup>-doped aluminosilicate melts, which are sufficiently viscous to be effectively suspended by refractory wire in a conventional furnace. Initial reaction morphologies match the cation-diffusion-dominated and rate-limited reduction dynamics articulated above; theoretical analysis/modeling of these dynamics are underway. The extension to inviscid liquids will be first approached on ferromagnesian orthosilicate, prepared by melting natural and synthetic ferromagnesian olivine,  $(Fe_x, Mg_{1-x})_2SiO_4$ . The control experiments on aluminosilicate and orthosilicate liquids will be extended to Aero Acoustic Levitation (AAL). The AAL experiments involve levitation on a gas jet of controlled oxygen activity, created by reacting mixtures of H<sub>2</sub> and CO<sub>2</sub> gasses. Initial levitation of specimens will be at an oxygen activity in which the material is stable against reduction; subsequent treatment will drive the reduction reaction.

The postulate for these experiments was founded on the results of oxidation studies of melts and glasses, previously supported by the NASA Microgravity Sciences program. In these earlier experiments, we were able to prove unequivocally the applicability of the "semiconductor condition" to the understanding of redox dynamics in iron-bearing aluminosilicate melts and glasses. Specifically, the polaron behavior decouples the diffusive motion of cations and anions; one consequence is that, when exposed to a gradient in the chemical potential of oxygen, the dynamic response allowing internal oxidation can avoid the motion of an oxygen species (ionic or

atomic/molecular) altogether. While we were able to demonstrate "isothermal undercooling" via oxidation that resulted in the uniform, internal heterogeneous nucleation of silicate phases on internal-oxidation-induced ferrite precipitates (homogeneously nucleated at the oxidation front), one difficulty was the coarsening of the ferrite nuclei. The dynamics of reduction should be the mirror-image, kinetically, of oxidation in such materials (our present work will confirm/deny this hypothesis).

Microgravity and containerless requirements merge in this research as both chemical and physical constraints of the surface condition are critical process parameters, as well as the need for quiescence in the melt droplet and the need to avoid gravity-effected separation of metal and ceramic liquid phases.

Understanding the dynamics of redox reactions in transition-metal-cation-bearing aluminosilicate melts, specifically because of this research, has already resulted in an important technological spin-off. We have recently successfully learned to push upward the maximum temperature for the "float" processing of silicate glasses (i.e., so as to form very flat sheet), from 1100 °C (the maximum temperature for float processing of soda-lime-silicate glass on pure molten tin) to approximately 1450 °C. The temperature transition allows the float processing of more refractory aluminosilicate compositions for application (e.g., in high-value-added flat-panel displays). The breakthrough required the combination of solution thermodynamics (the float medium is an exothermic, liquid metallic alloy) with the ability to control, by appropriate doping, the chemical diffusion process in the silicate melt that allows for its reduction.

The results of this present melt-reduction research will also impact our understanding of our solar system: the reduction morphology witnessed in chondrules in the most primitive chondritic meteorites (natural microgravity processing of ceramic melts) is similar to that seen in our preliminary experiments. We may, thus, be able to articulate thermodynamic/kinetic constraints on the evolution of the protosolar nebula.